Microscopic Strain Mapping in Nanostructured and Microstructured Alumina-Titania Coatings Under 4-point Compressive and Tensile Bending

A. Ignatov[1,2], E. K. Akdogan[1], N. Ahmedi[1], L. Balarinni[1], Z. Zhong[3],
M. Croft[2,3] and T. Tsakalakos[1]

[1] Department of Materials Science and Engineering, Rutgers University, Piscataway, NJ 08854
[2]Department of Physics, Rutgers University, Piscataway, NJ 08854
[3]National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973

Acknowledgments: The financial support of Office of Naval Research under grant N000140610880 is gratefully acknowledged. Samples were prepared by A&A Co.

E-mail: aignatov@rci.rutgers.edu

Engineering Conference International, Sub-Micron & Nanostructured Ceramics
Colorado Springs, June 7-12, 2009, Colorado, USA

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
JUN 2010	**N/A**	**-**

4. TITLE AND SUBTITLE
Microscopic Strain Mapping in Nanostructuredand MicrostructuredAlumina-TitaniaCoatings Under 4-point Compressive and Tensile BendingA

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Tsakalakos11Department of Materials Science and Engineering, Rutgers University, Piscataway, NJ 088542Department

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
See also ADM002307. ECI International Conference on Sub-Micron and Nanostructured Ceramics Held in Colorado Springs, Colorado on 7-12 June 2009, The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**UU**	**35**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Outline

- Background and objectives
- Synchrotron EDXRD strain mapping
- Results of microscopic strain mapping of n- and μ- coatings at high loads
- Continuous local cracking behavior in over coated n- and μ- specimens under small tensile loads
- Results of optical and electron microscopy studies
- Models of nonlinear behavior in tension
- Conclusions

Background

1) Properties of Alumina-Titania coatings:

- Corrosion resistance, including resistance to build-up of deposits from sea salts;
- Mechanical wear resistance;
- Spallation / cracking / chipping resistance;
- Strain tolerance

2) Real life application: (Courtesy of Dr. Ken Scandell, Naval Surface Warfare Center)

Ship shaft failed after 18 months of service requiring dry docking.

Uncoated shaft experiences severe scoring damage

No visible damage after four years of service

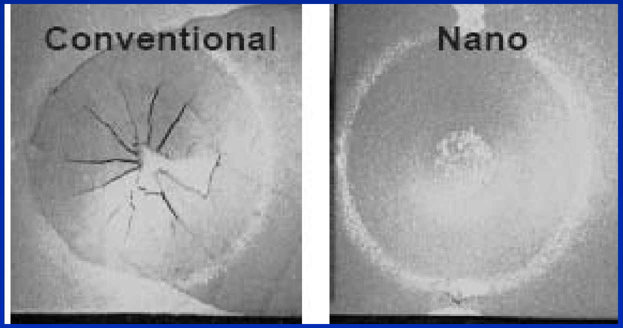
3) Two types of coatings will be considered:

- Metco 130 (Al_2O_3-13wt%TiO_2 , commercial micro coating) referenced as micro coating
- Nano coating (i.e used by A&A LTD) developed at UCon in 1990s, references as nano coating

Background (continued)

"*Fabrication and evaluation of plasma sprayed nanostructured alumina-titania coatings with superiour properties*", by E.H. Jordan, M. Gell, Y.H. Sohn, D. Goberman, L. Shaw, S. Jiang, M Wang, T.D. Xiao, Y Wang, and P. Strutt, *Materials Science and Engineering* A**301** (2001) 80.

Superior mechanical properties were achieved including indentation crack resistance, adhesion strength, spallation resistance against bend- and cut test, abrasive wear resistance, sliding wear resistance.



Typical cup tests results for Melco-130 (conventional) and nano coatings

XRD, SEM, TEM experiments were conducted.

The superior mechanical properties of nano coatings are attributed to constituent phases and microstructure: the nano coatings microstructure is bimodal in nature. It consists of regions of fully-molten (FM) splats (nanocrystaline γ-Al_2O_3) interspersed with partially-molten (PM) domain (~20-50 μm in diameter, Ti-rich amorphous phase with α-Al_2O_3 grains of ~1 μm in diameter).

Objectives

- Professor T.W. Clyne (Materials Science and Metallurgy, U of Cambridge, UK) "…in very few studies have reliable correlations been established among process conditions, measured stress levels, and indicators of coating performance."

  Residual Stresses in Thermal Spray Coatings and Their Effect on Interfacial Adhesion: A Review of Recent Work, J. of Thermal Spray Tech., v5 (1996) 401
- The interaction between residual stresses (incurred during fabrication or duty to duty cycle fatigue) and applied stresses accounts for the failure of most structural engineering elements.
- Many powerful techniques in this area are explicitly destructive and involve theoretical modeling of the strain fields accompanying material removal (e.g. hole drilling and layer removal). XDR, FTIR, and Raman are surface sensitive.

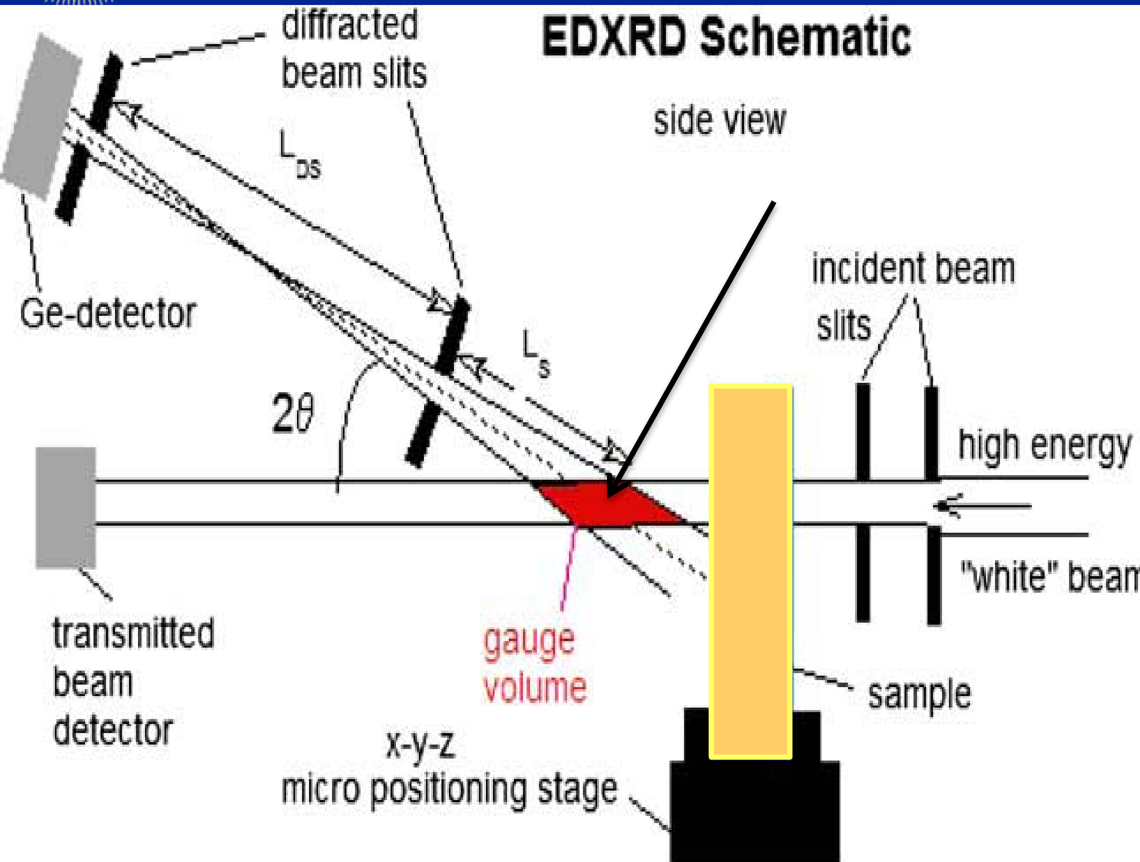
This work is undertaken to

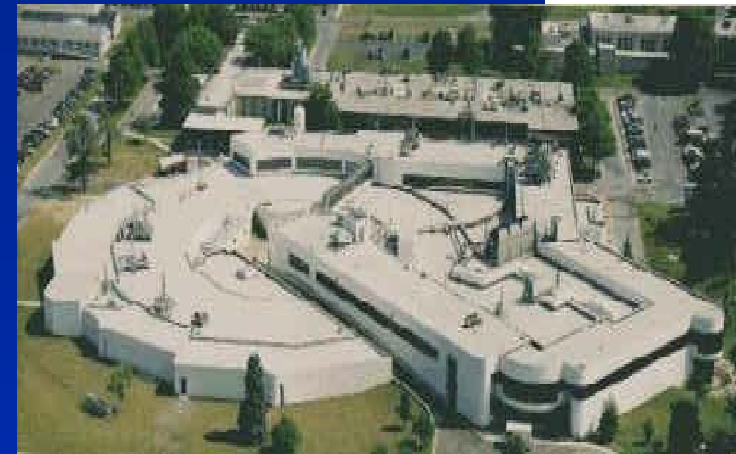
(1) Measure experimentally microscopic strains across the entire specimens (n- and μ-alumina-titania coatings sprayed on grit-blasted Ti substrates with bond layers) as a function of 4-point bending moment using energy dispersive x-ray diffraction (EDXRD);

(2) Establish correlations between measured stresses and coating performances;

(3) Based on the gained understanding come up with recommendations on fabrication and duty cycle conditions.

EDXRD set up, Rutgers at the NSLS-I

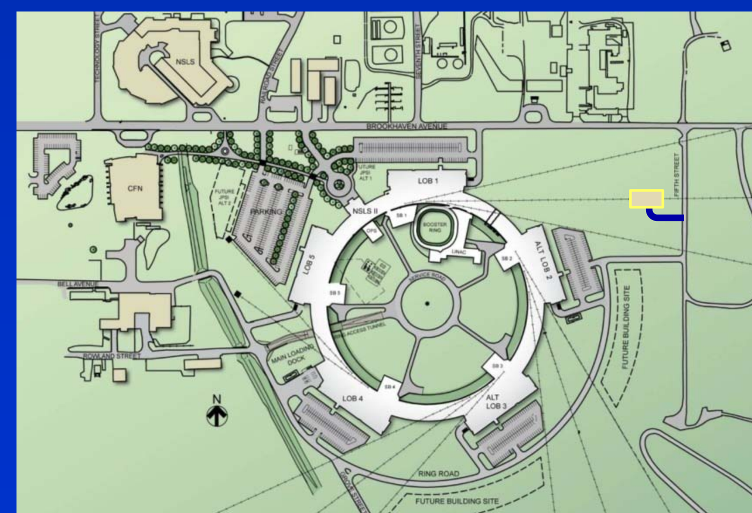




Current source of the x-ray beam: the NSLS-I (www.nsls.bnl.gov)

We measure high energy diffraction from a fixed Gauge Volume (GV) defined by fixed angle 2θ and slits

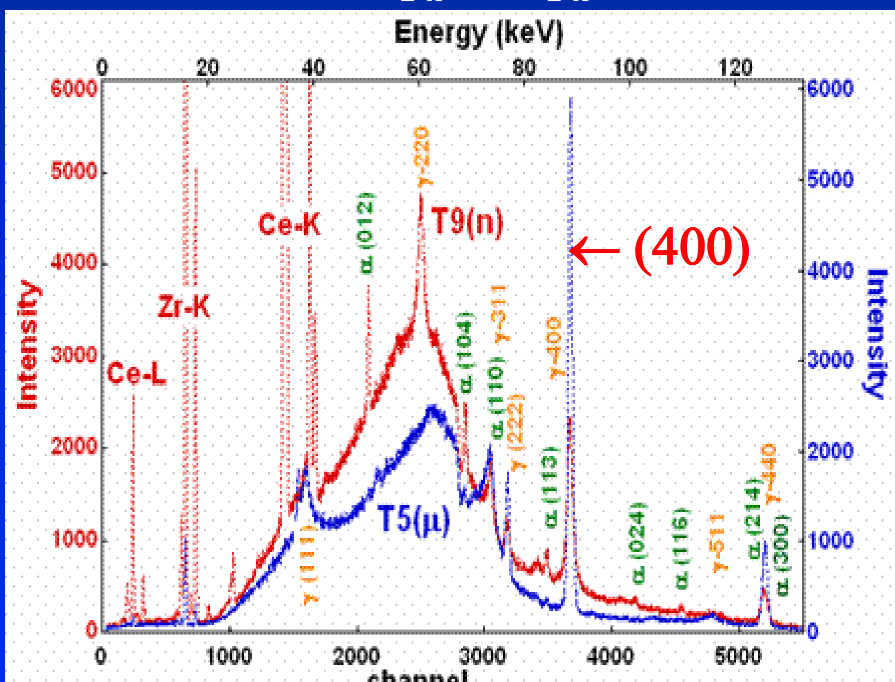
- **Beamline X17-B1 at the NSLS, Brookhaven Natl Lab**
- **White radiation up to 200 keV from SC Wiggler**
- **Fixed 2θ, 2-12°, typically 4°**
- **GV's typical L x W x H = $10^4 \times 60 \times 100\ \mu m^3$**
- **Average over 10-80 x 10^3 grains in the GV**



NSLS-II, www.bnl.gov/nsls2/project/

EDXRD patterns of n- and μ- coatings

- γ-400 Bragg line of the $\gamma\text{-}Al_2O_3$ spinel phase will be used for the strain mapping in both n- and μ- coatings
- Note that in the in nano material:
- $\alpha\text{-}Al_2O_3$ corundum phase is present
- grain size is smaller;
- Ce and Zr atomic fluorescence indicates extra phases ($CeO_{2\text{-}x}$, $ZrO_{2\text{-}x}$)



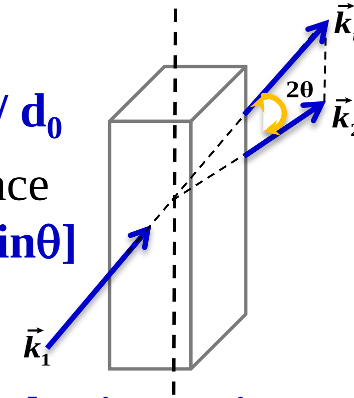
Indexed EDXRD patterns in micro (T5) and nano (T9) coating powders

Strain, by definition is

$\varepsilon(hkl)= [d(hkl)-d_0(hkl)] / d_0$

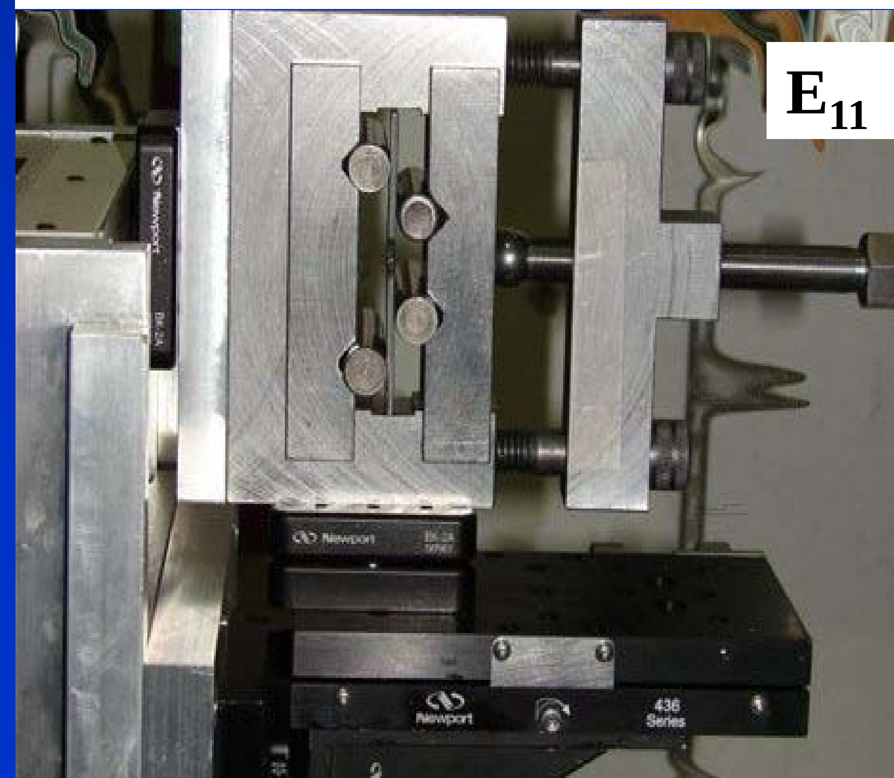
Bragg's equation in E-space

$E(hkl) = 6.199 / [d(hkl)\sin\theta]$

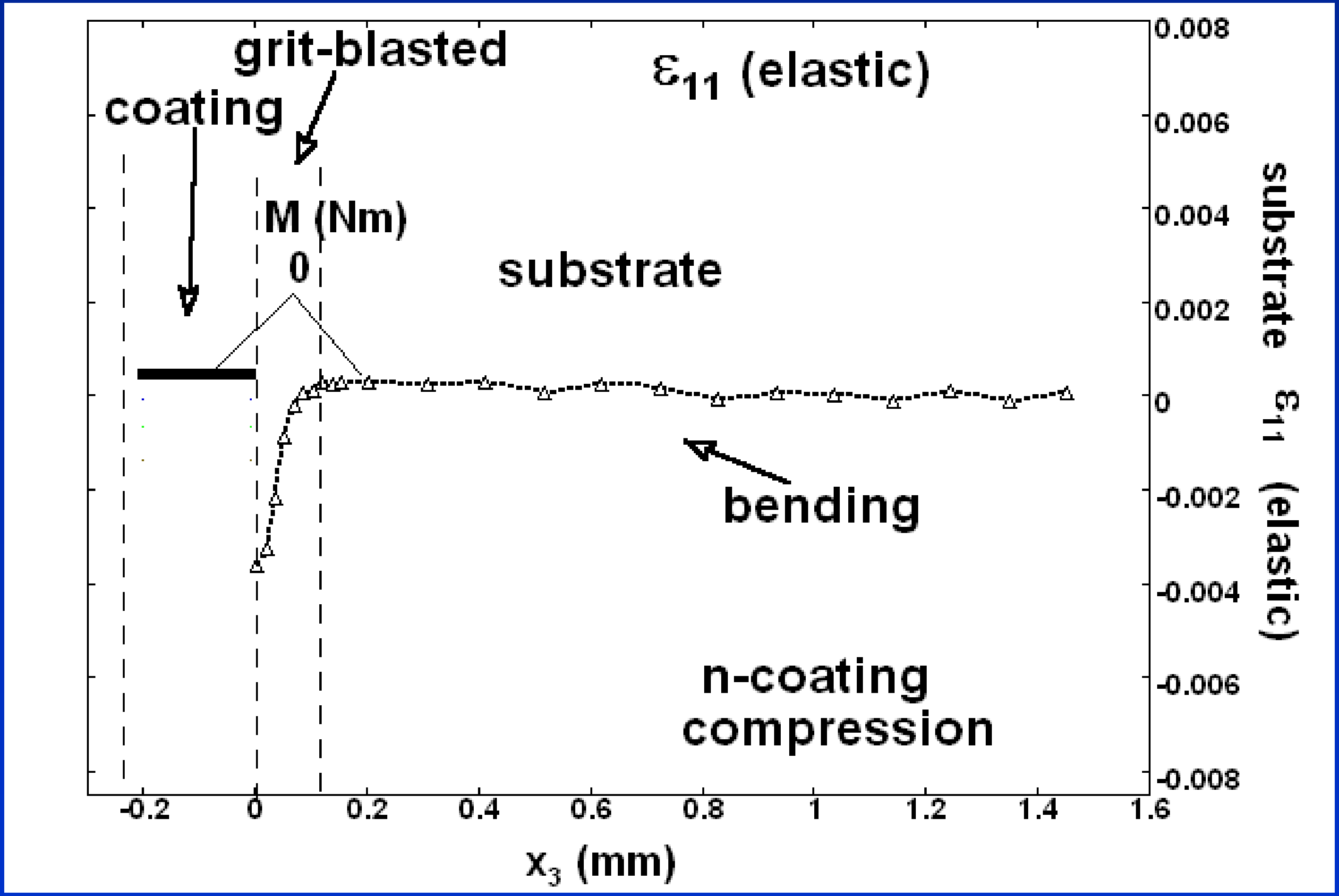


$\varepsilon(hkl)= [E_0-E(hkl)] / E_0$

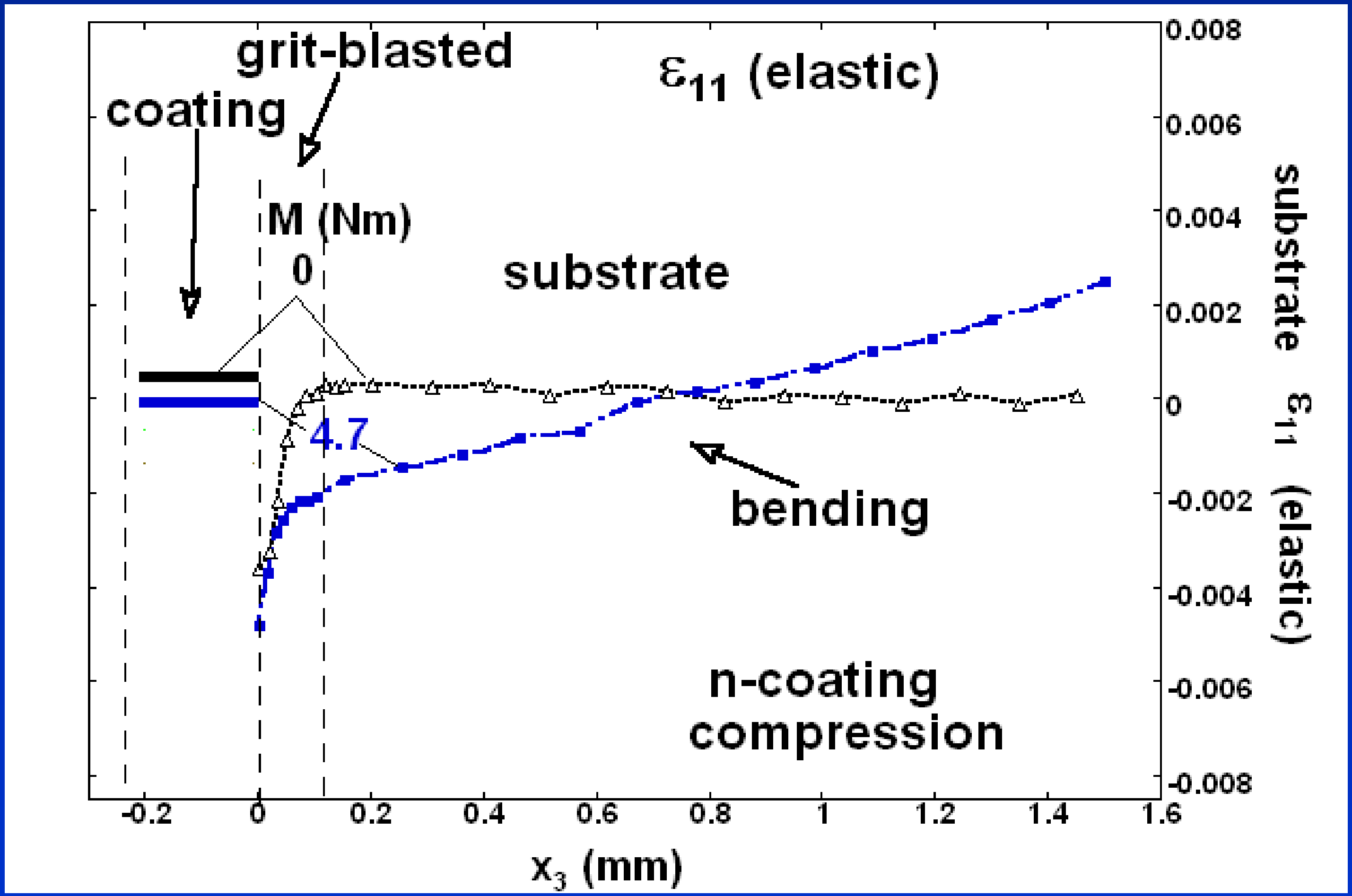
EDXRD measures only Elastic Strain



Can strain in ceramic coating be seen with EDXRD ?

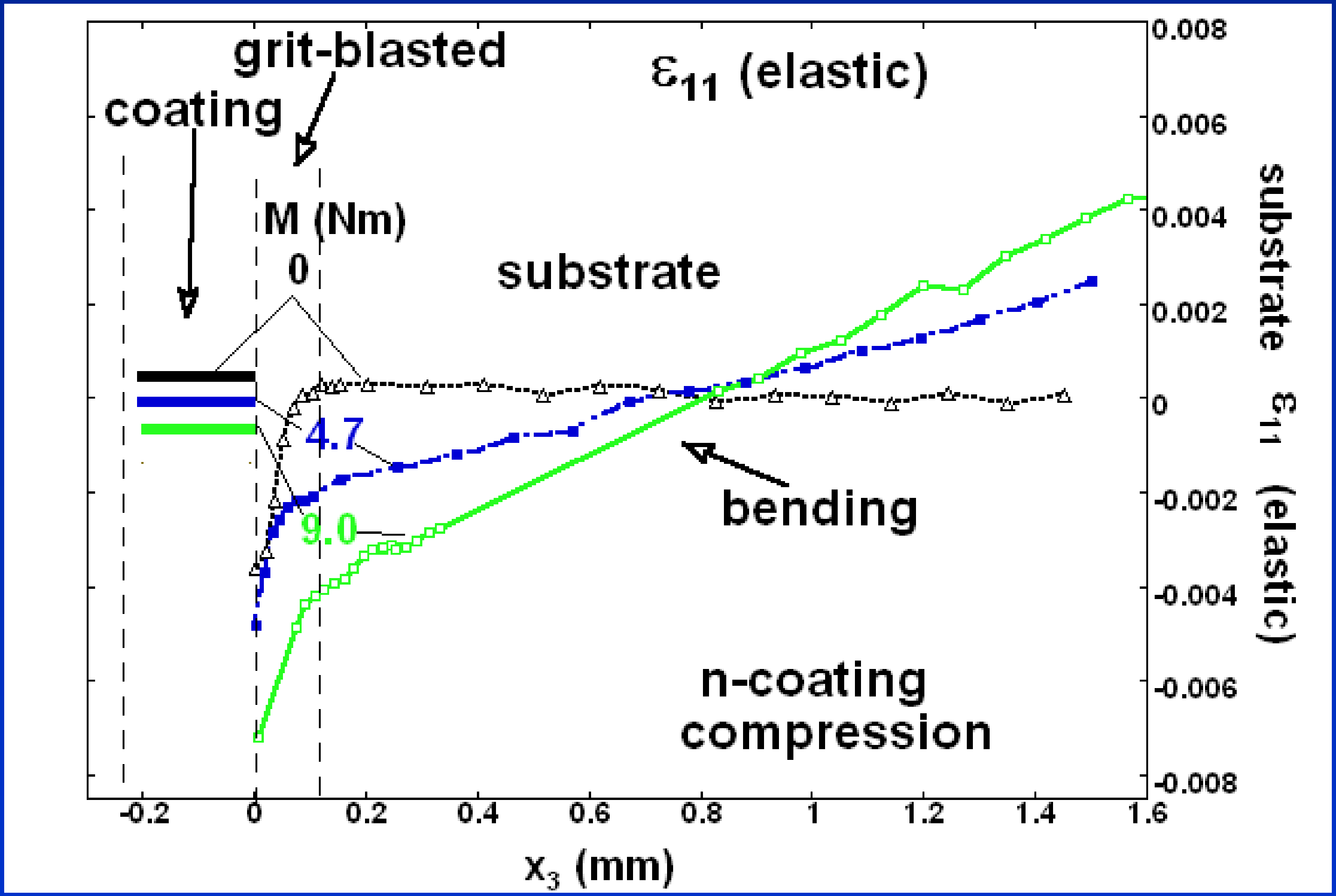


Can strain in ceramic coating be seen with EDXRD ?



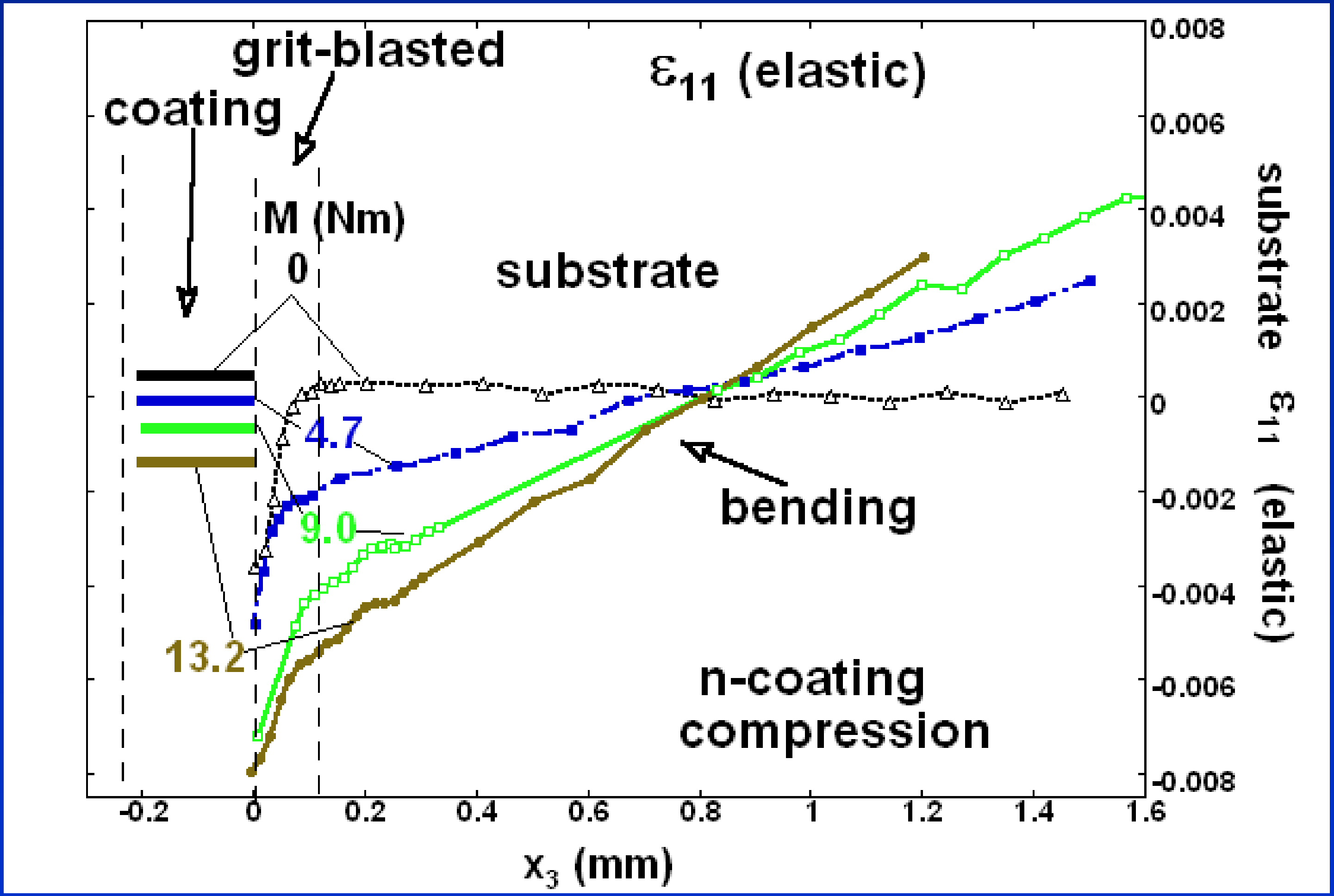
Both coating and substrate respond to compressive load of 4.7 Nm

Can strain in ceramic coating be seen with EDXRD ?



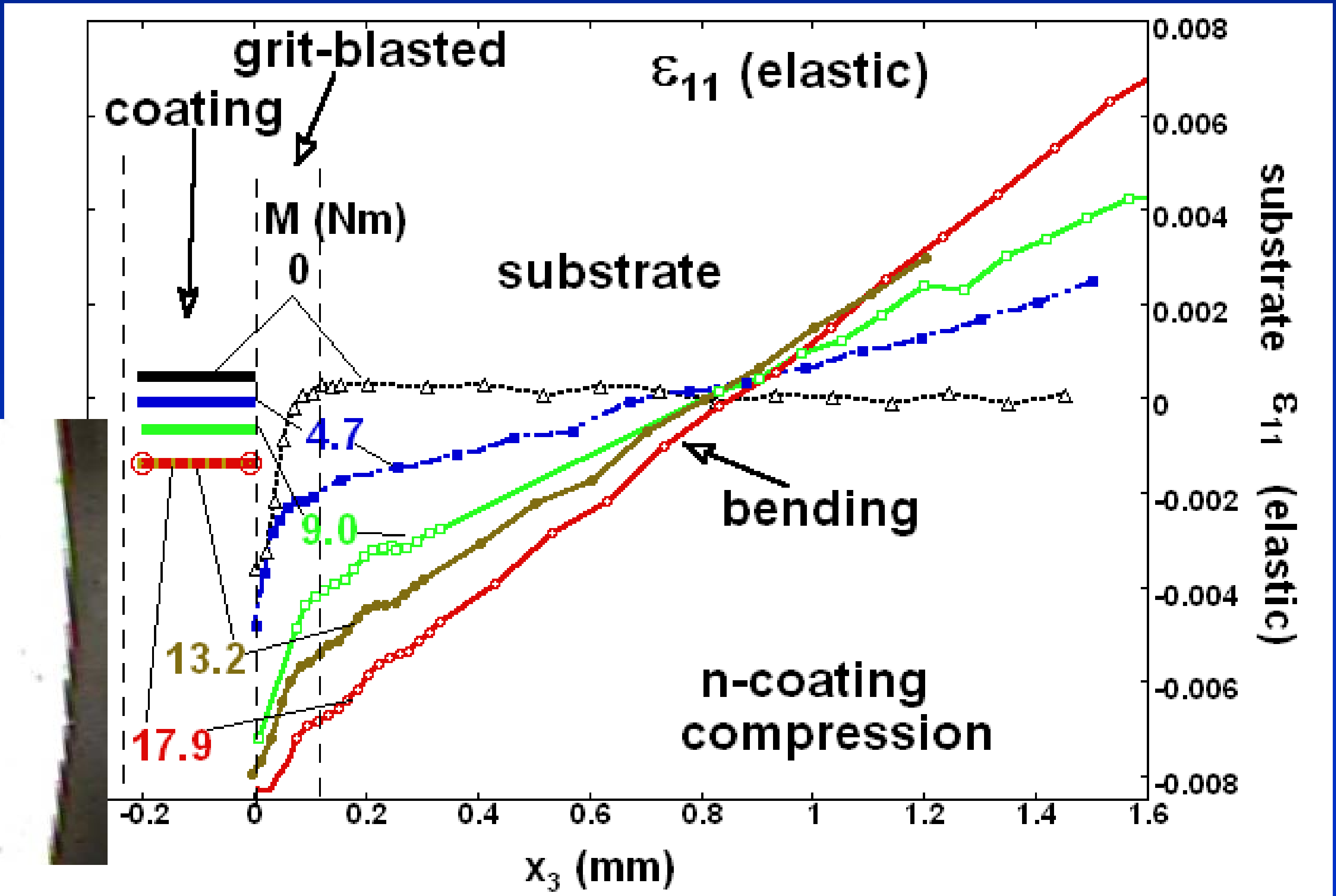
Both coating and substrate respond to compressive load of 9.0 Nm

Can strain in ceramic coating be seen with EDXRD ?



Both coating and substrate respond to compressive load of 13.2 Nm

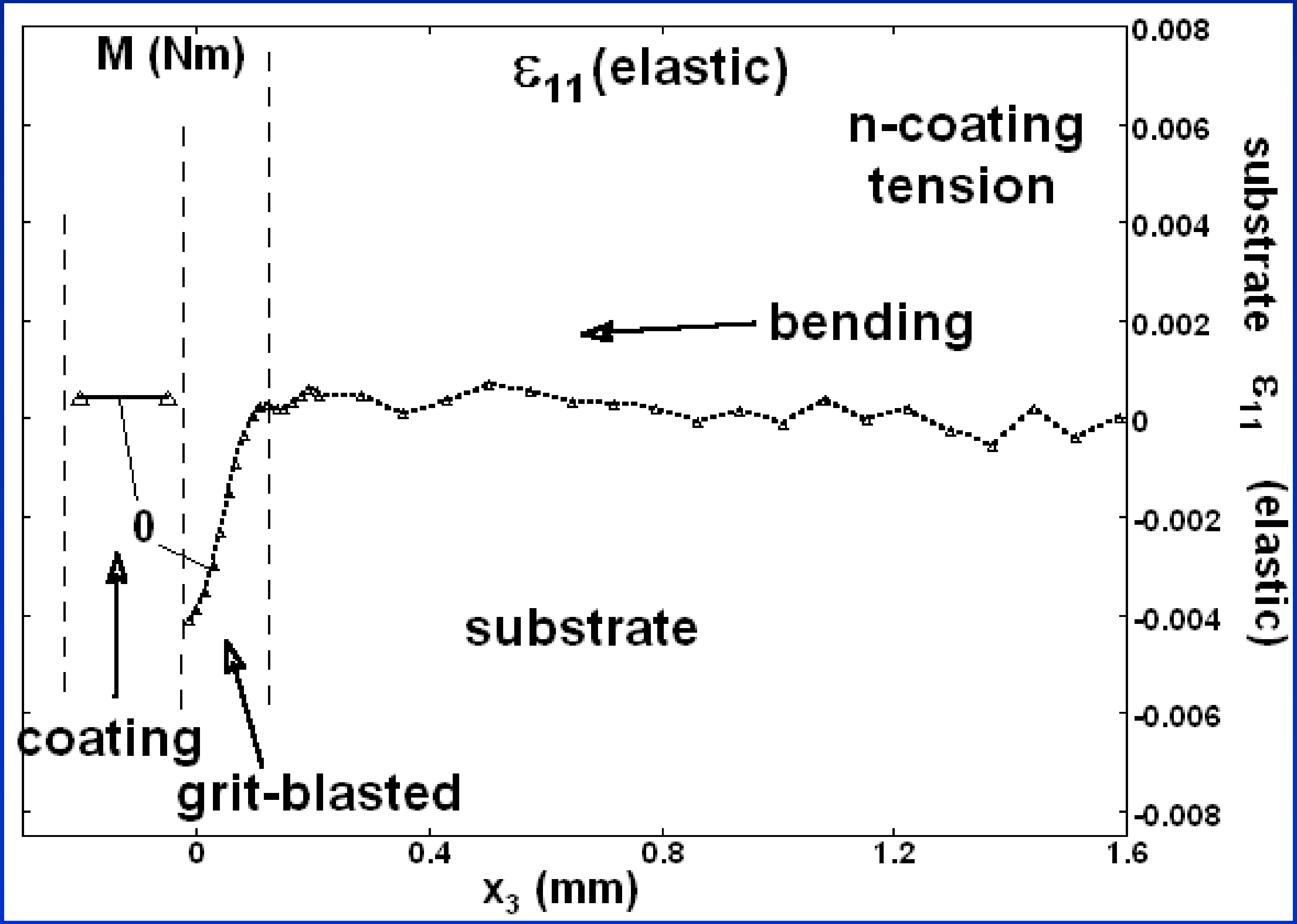
Can strain in ceramic coating be seen with EDXRD ?



Coating fracture

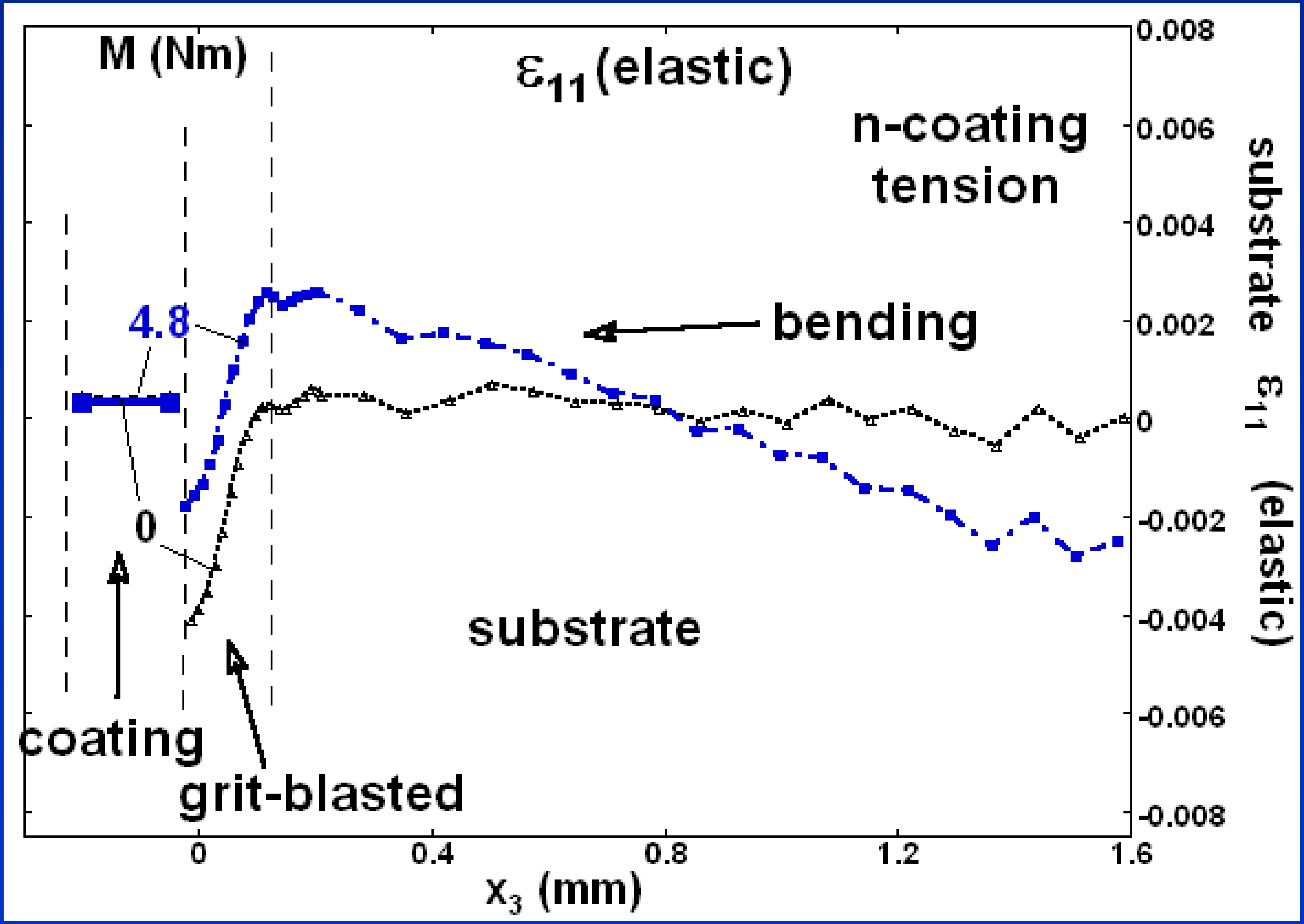
Coating does not respond to compressive load of 17.9 Nm, while substrate does

Will ceramic respond under tensile loads ?



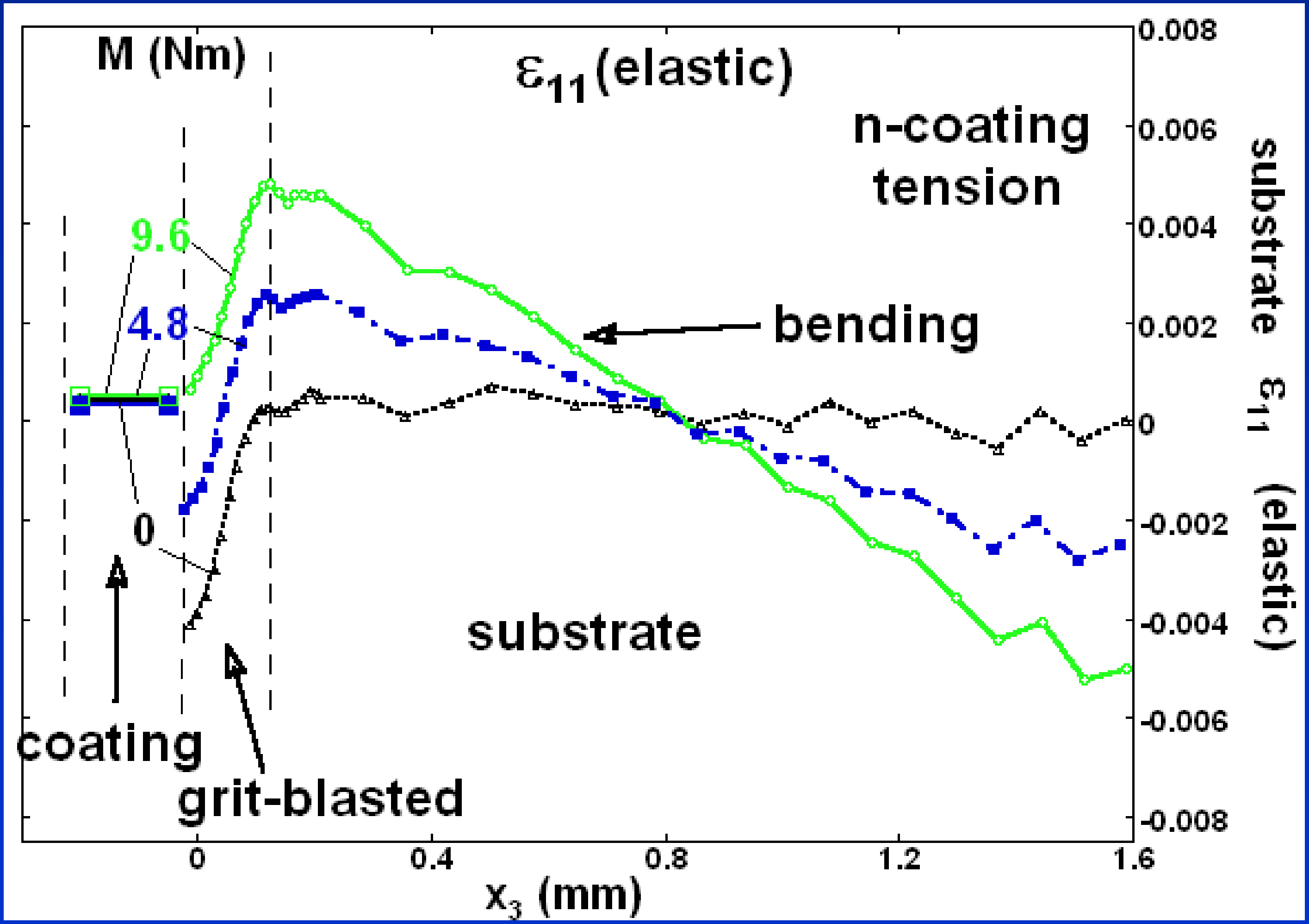
Zero load

Will ceramic respond under tensile loads ?



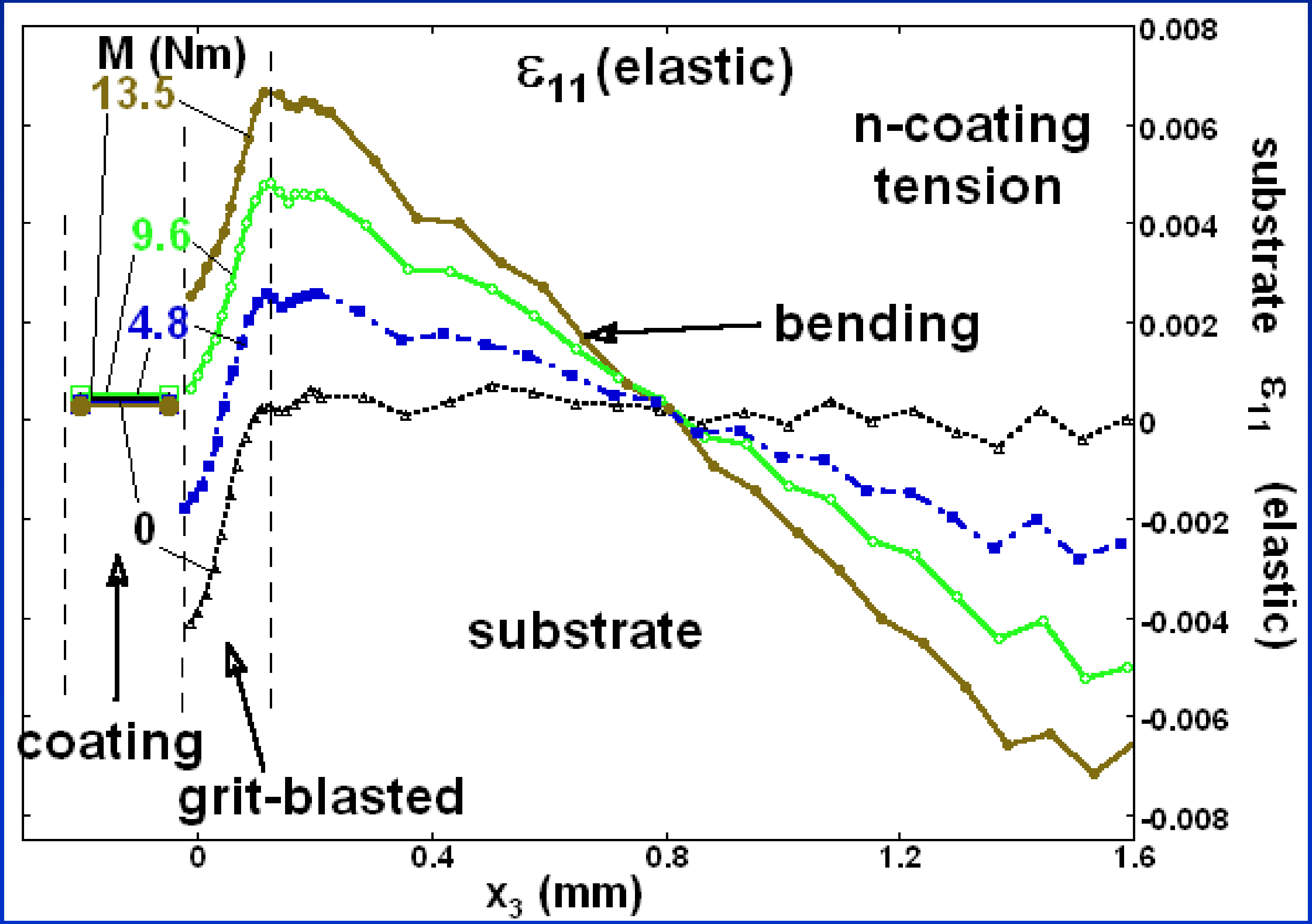
Coating DOES NOT respond to compressive load of 4.8 Nm, while substrate does

Will ceramic respond under tensile loads ?



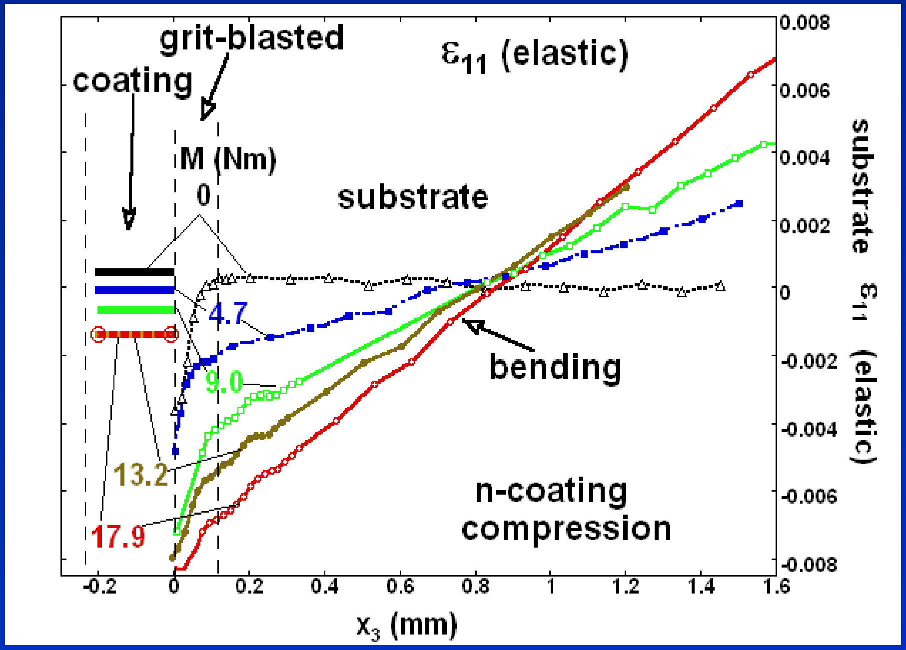
Coating DOES NOT respond to compressive load of 9.6 Nm, while substrate does

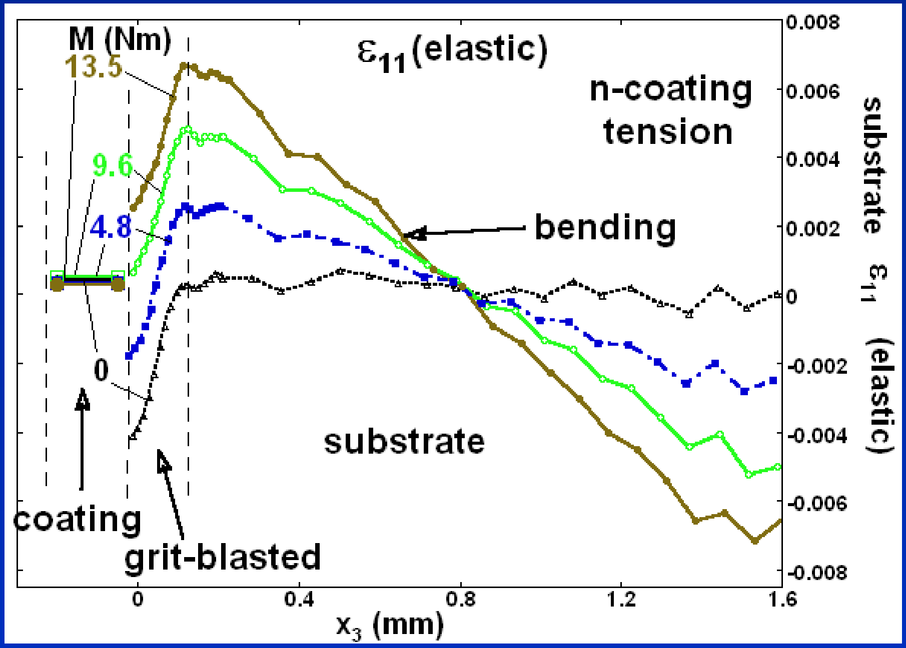
Will ceramic respond under tensile loads ?

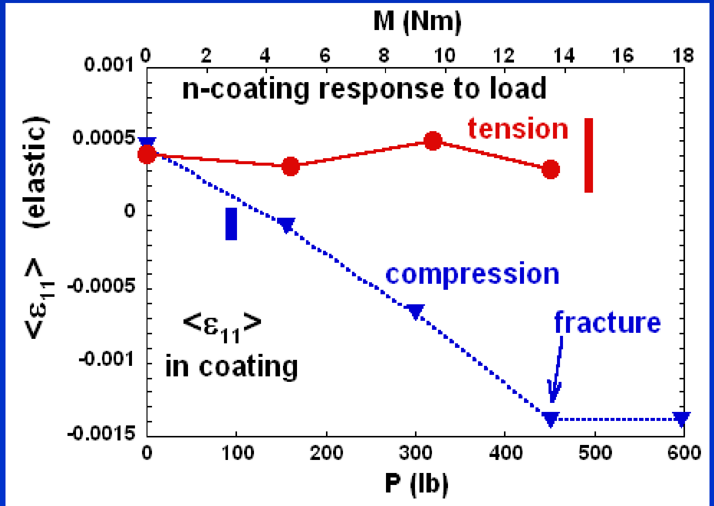


Coating DOES NOT respond to compressive load of 13.5 Nm, while substrate does

Summary: n- coatings at high compressive and tensile loads





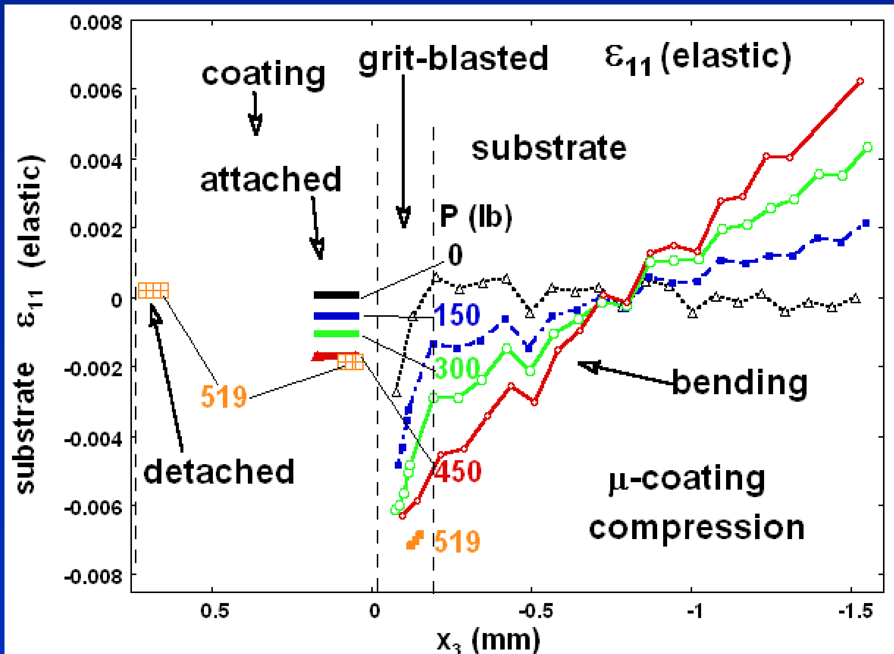


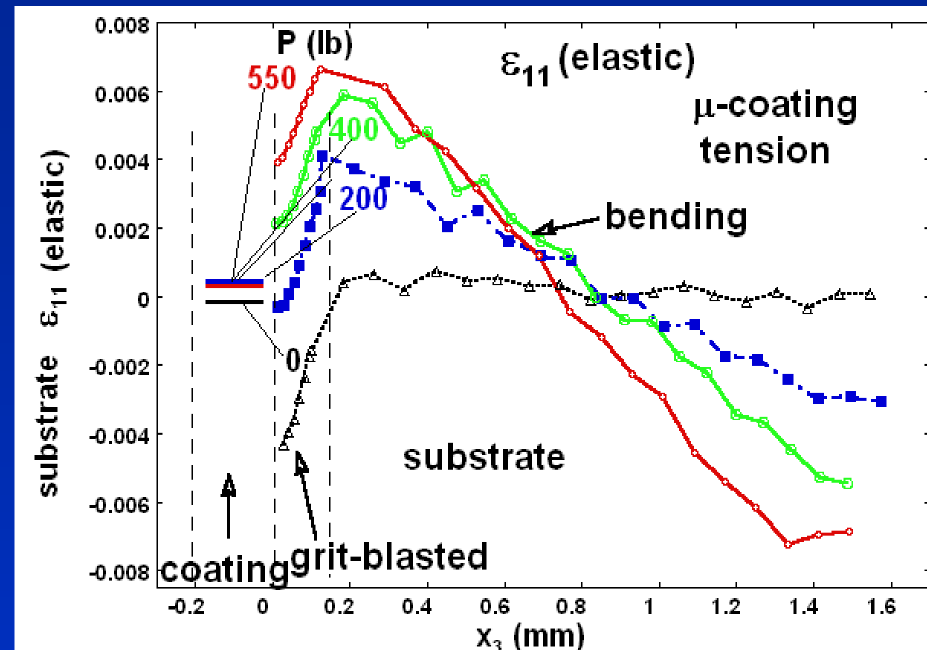
(a) Elastic response in compression until coating fractures

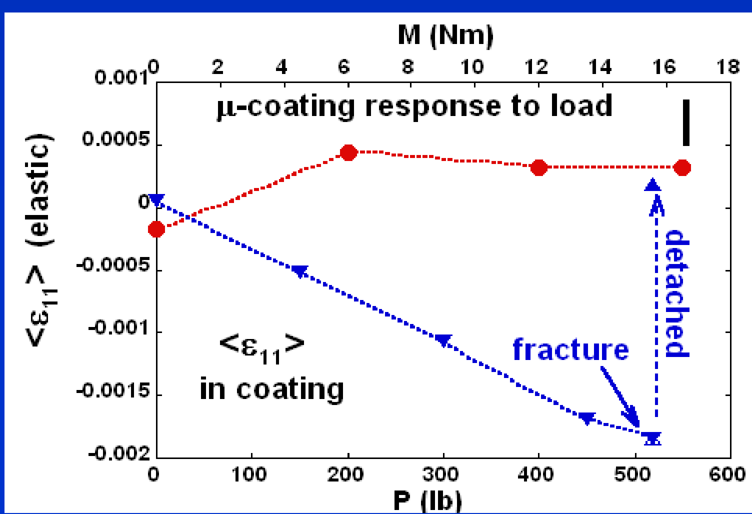
(b) Compressive yield strain is about -0.15%

(c) No obvious elastic response in tension

Summary: μ- coatings at high compressive and tensile loads





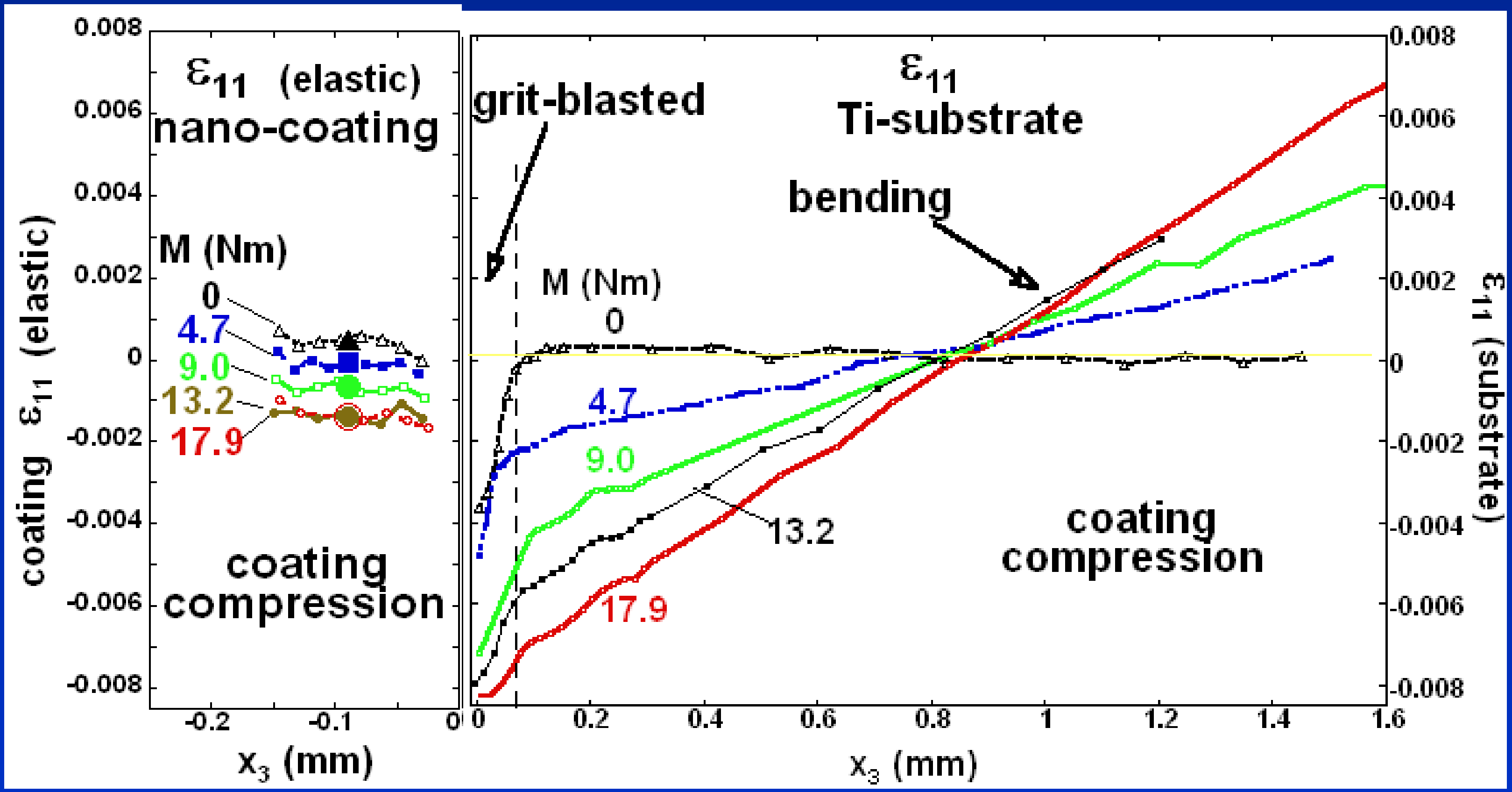


(a) Elastic response in compression until coating fractures. Strain relaxes in delaminated part

(b) Compressive yield strain is about -0.18%

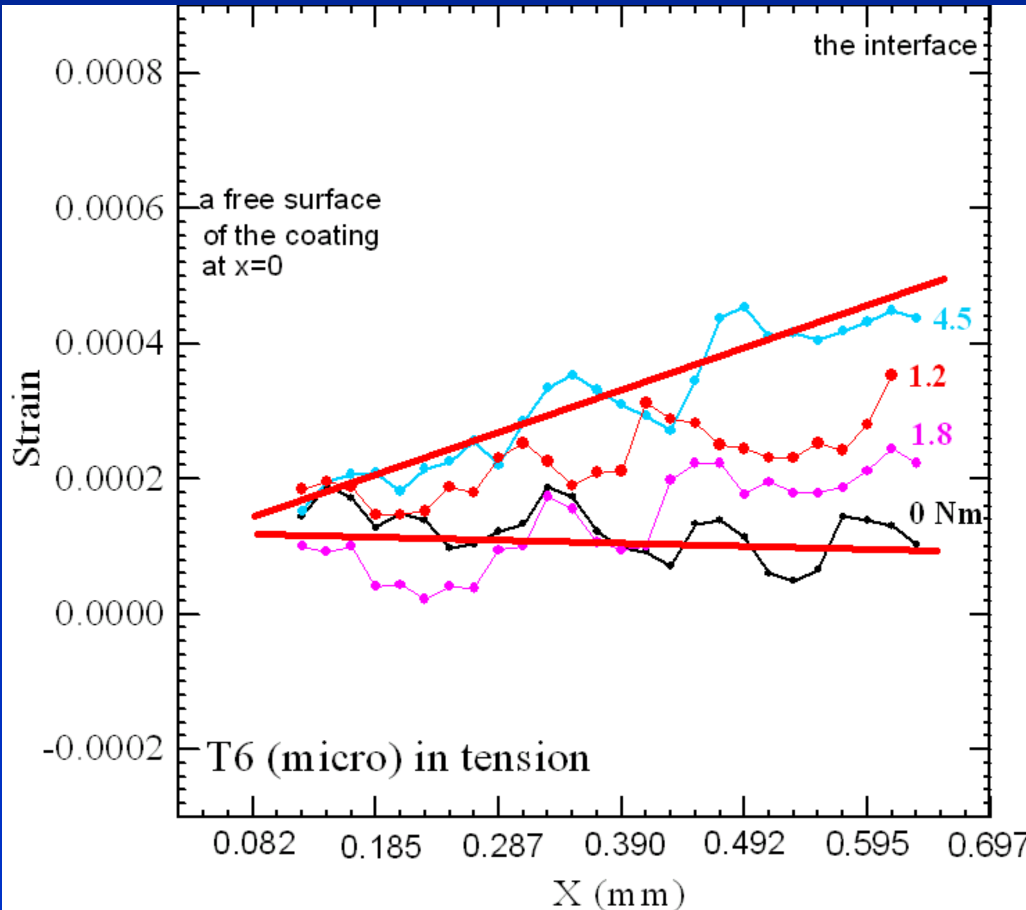
(c) No obvious elastic response in tension

Technical note on showing Strain vs. X in the coatings



Strain in the coatings was shown as an average of the $\varepsilon(x)$.

Low loads: a strain profile in μ- coating



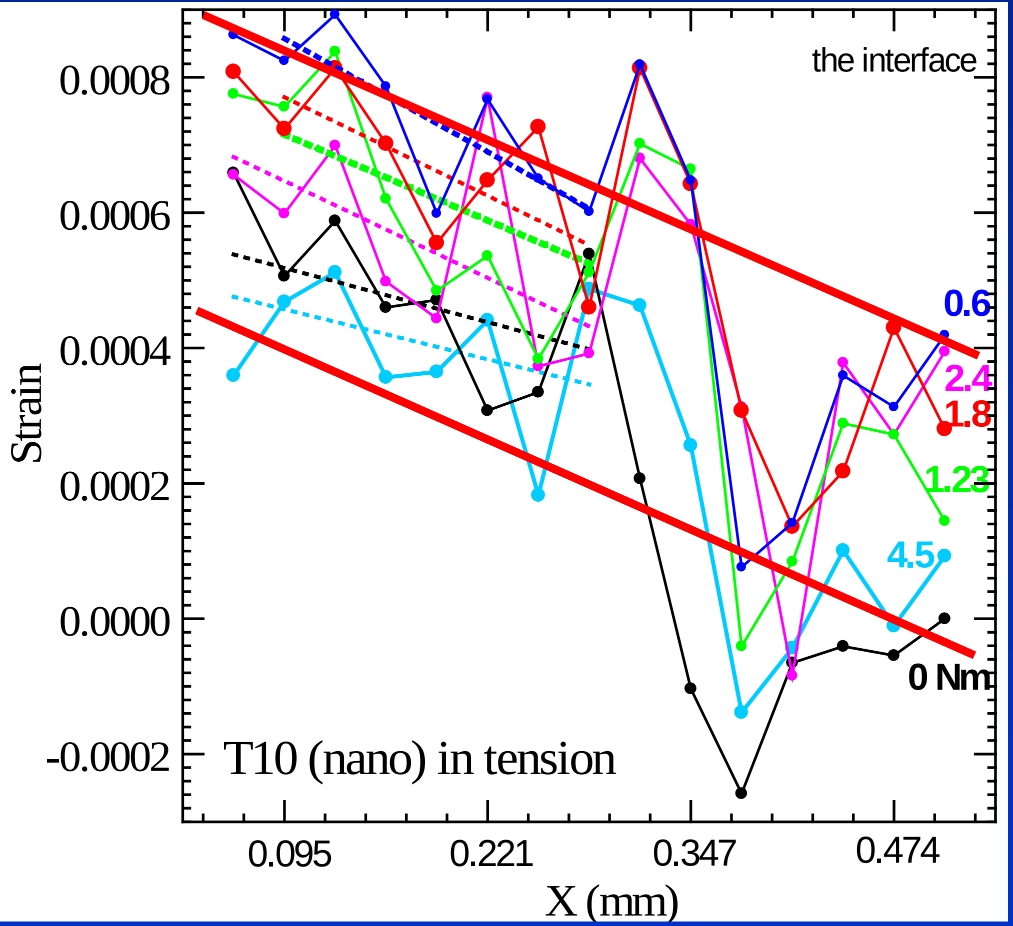
(1) Strain relaxes towards the free surface of the coating;

(2) Strain spans area between two red curves showing stochastic fluctuations as function of applied loads (a signature of a continuous local cracking);

(3) Max value of the strain that the studied micro coating is capable of supporting is ~0.04%. This is a microscopic yielding strain in tension ;

(4) Oscillating behavior is attributed to underlying microstructure due to plasma spraying;

Low loads: a strain profile in n- coating



(1) Strain distribution is uniform across the n- coatings;

(2) Compressive type of slope is retained over whole range of loads;

(3) Strain spans rectangular area between two red curves showing stochastic fluctuations as function of applied loads;

(4) Max value of the strain that nano coating is capable of supporting is ~0.08% (approximately twice as large as in the micro coating).

(4) Underlying macrostructure due to plasma spraying is apparent, including large inclusion at x~0.4;

I. Making rational of local strains: SEM and optical microscopy :

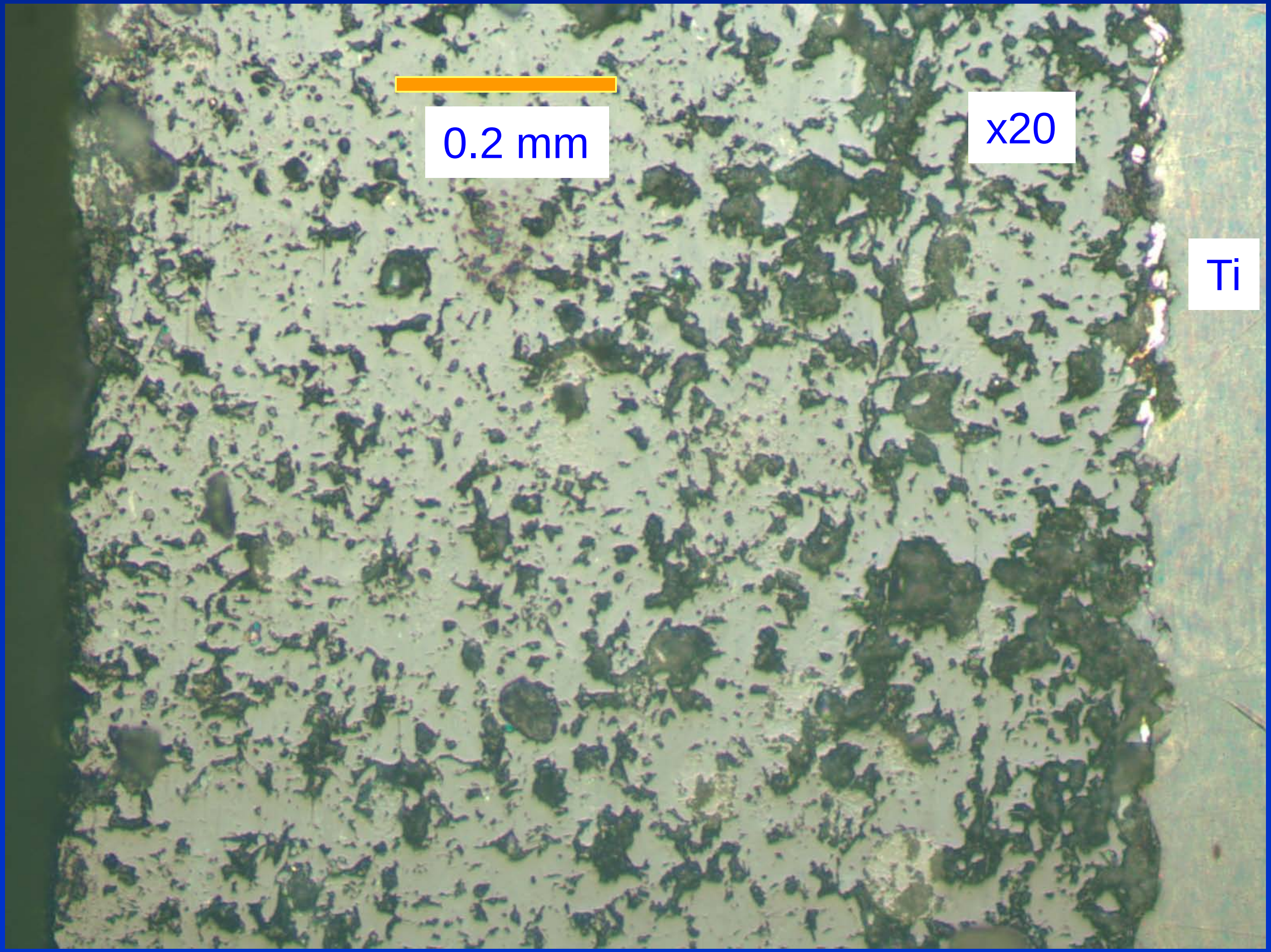
In n-coatings the observed strain distribution would be consistent with micro cracks being spread uniformly across the coatings pinned by inclusions and unable to propagate far enough or link with other cracks.

In μ- coatings the observed strain distribution would be consistent with higher density of cracks and/or linking micro-cracks to macro-cracks towards the surface of the coating.

SEM and optical microscopy are in order to visualize the cracks at different length scales and to correlate the crack distribution to the strain field via appropriate modeling

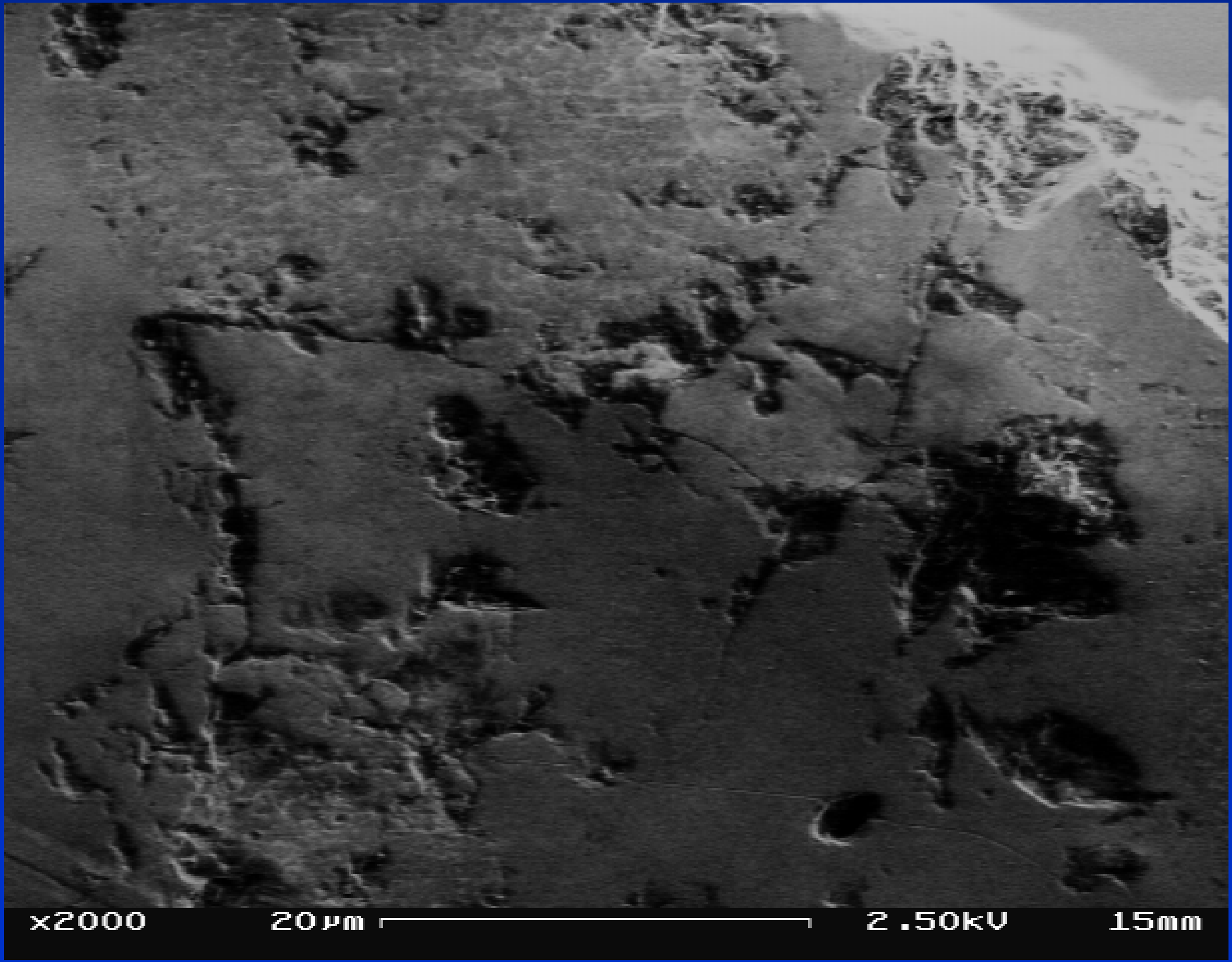
Cross-sectional optical micrographs of the μ- coating

Cross-sectional optical micrographs of the n-coating



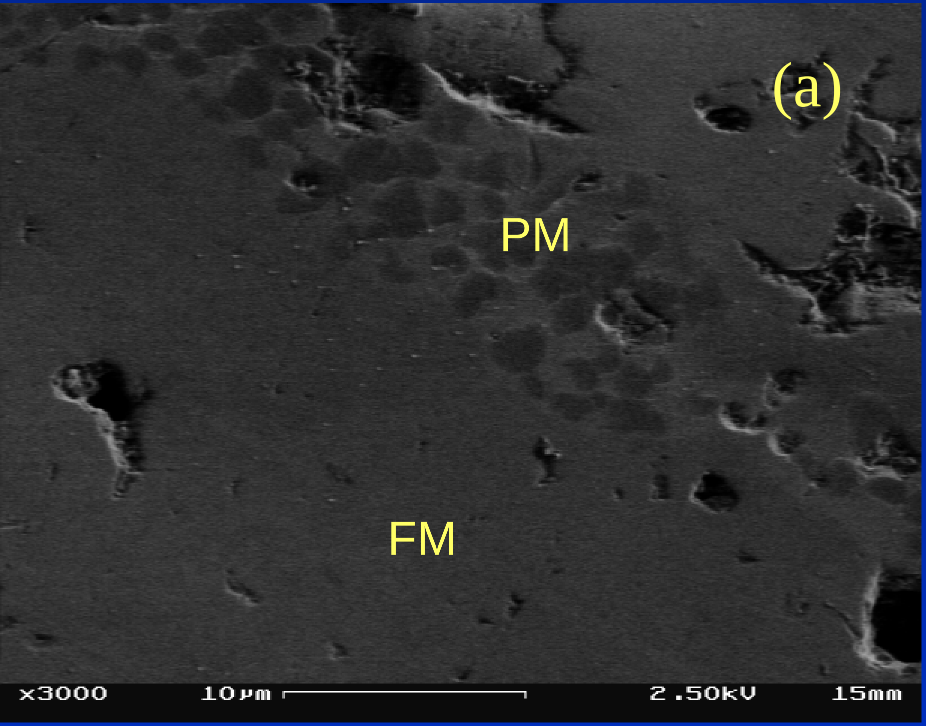
NO visible macro cracks

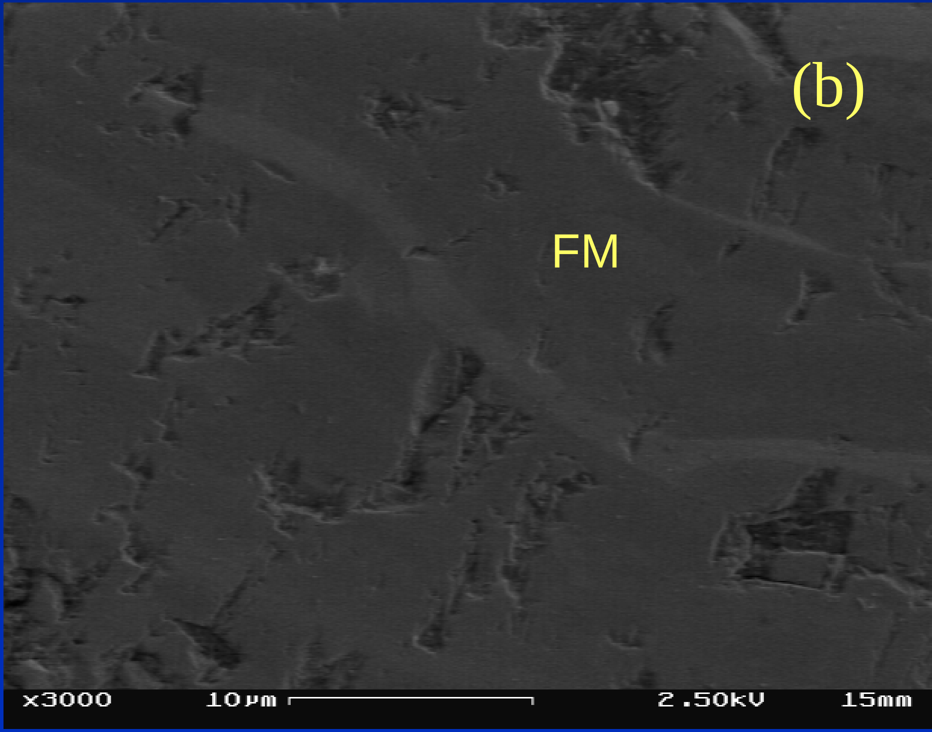
SEM micrograph of the n- coating close to its surface



Though macro cracks are not observed (previous slide), micro cracks are easily seen

Microstructure of n- and μ- coatings from SEM :





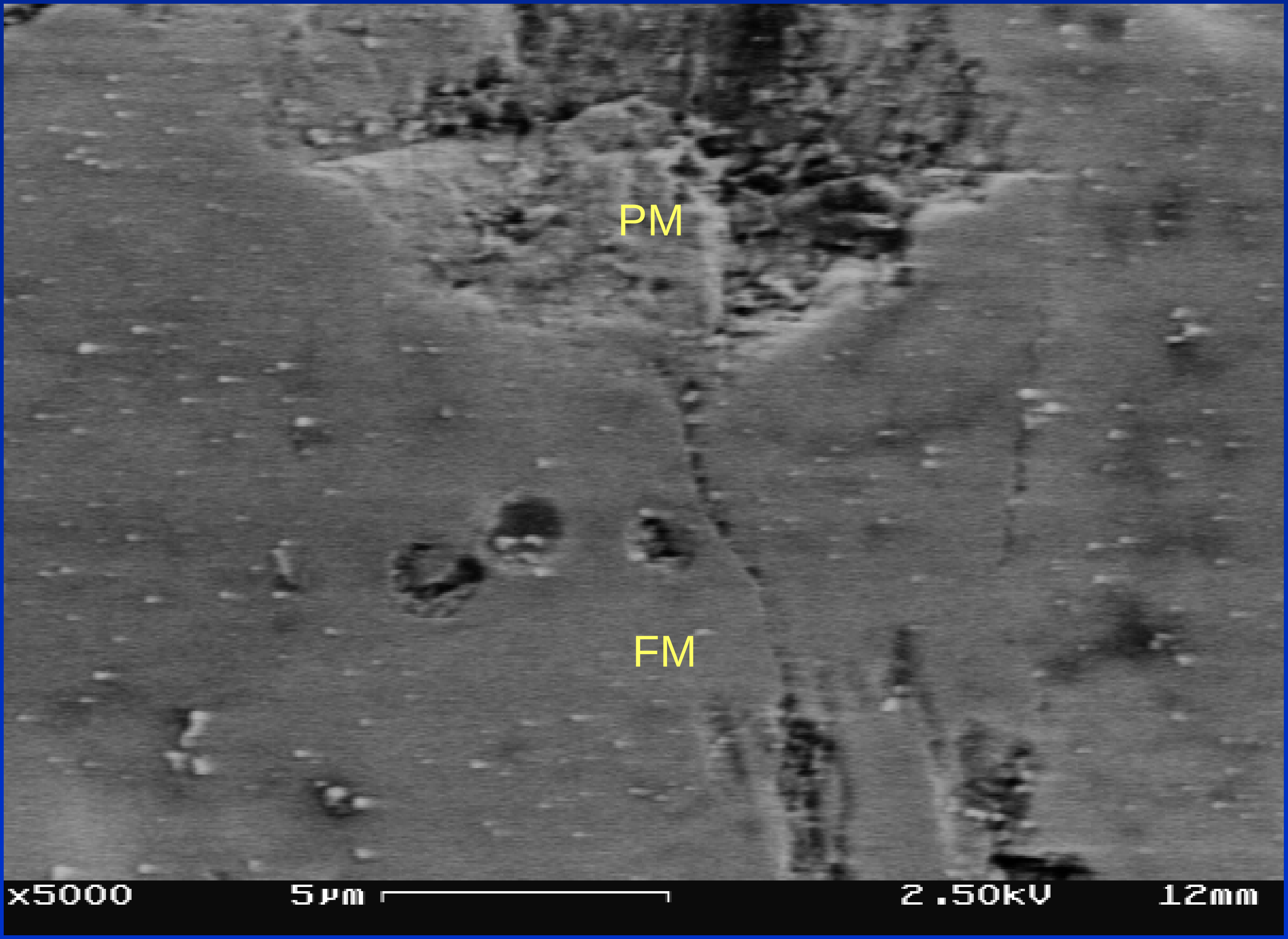
Cross-sectional SEM micrographs of nino (a) and micro (b) coatings.

- The nano coating microstructure is bi-modal. It consists of regions of fully-molten (FM) splats (nanocrystaline γ-Al_2O_3) interspersed with partially-molten (PM) domain ~20-50 μm in diameter, Ti-rich amorphous phase with α-Al_2O_3 grains of ~1 μm in diameter (black inclusions).

-The micro coating microstructure is uni-modal. It consists of FM splats

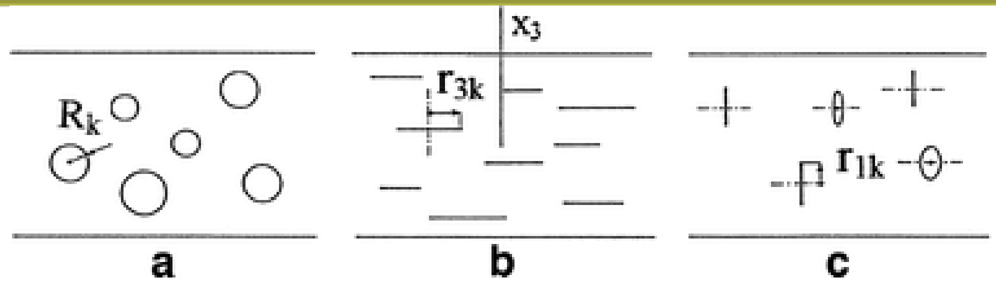
The assessment on phase and element composition is based on TEM and EDX measurements by D. Goberman, Y.H. Sohn, L. Shaw, E.H. Jordan, M. Gell, *Acta Mater*, v**50** (2002) 1141.

Microcrack arrests by the inclusion in the nano coating



Partially-molten domain with α-Al_2O_3 grains stops the crack propagating from the bottom

Theory: Young's moduli renormalization



Models of defects structure: (**a**) spherical pores, (**b**) horizontal, and (**c**) vertical microcracks, after F. Kroupa & M. Kachanov, 1998

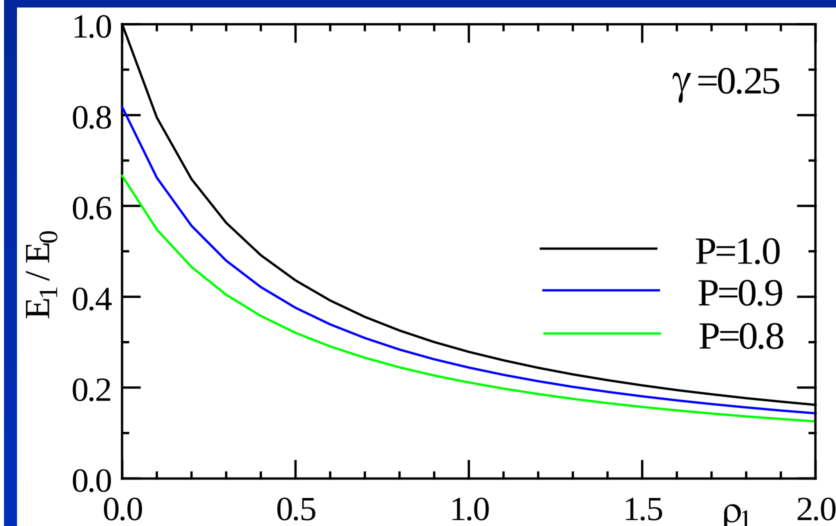
$$P = \frac{1}{V}\sum_{i=1}^{N}\frac{4\pi}{3}R_i^3 \qquad \rho_1 = \frac{1}{V}\sum_{k}^{M} r_{1k}^3 \qquad \rho_3 = \frac{1}{V}\sum_{k}^{L} r_{3k}^3$$

$$E_1 = \frac{E_0}{\left\{1 + c_1\dfrac{P}{(1-P)} + a_1\dfrac{\rho_1}{(1-P)}\right\}}$$

$$E_3 = \frac{E_0}{\left\{1 + c_3\dfrac{P}{(1-P)} + a_3\dfrac{\rho_3}{(1-P)}\right\}}$$

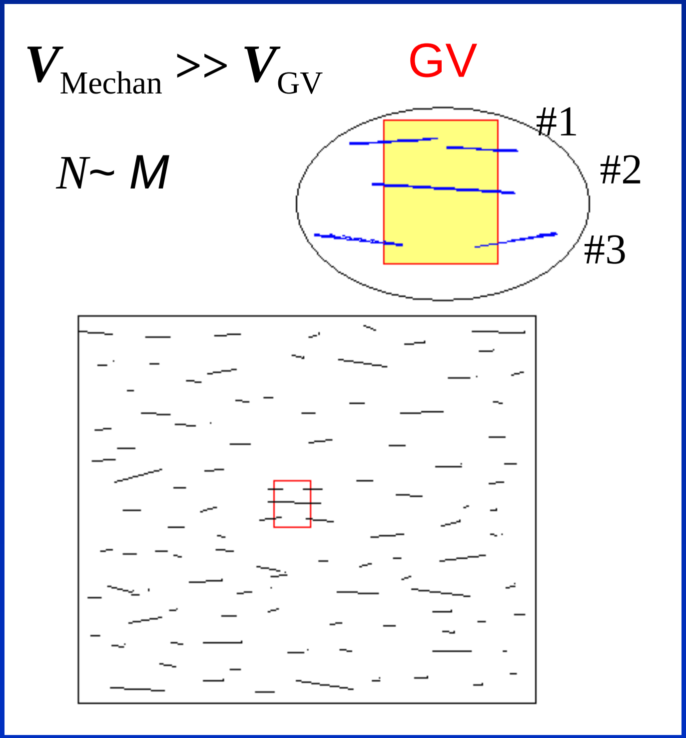
$$c_1 = c_3 = \frac{3(1-\gamma)(9+5\gamma)}{2(7-5\gamma)}$$

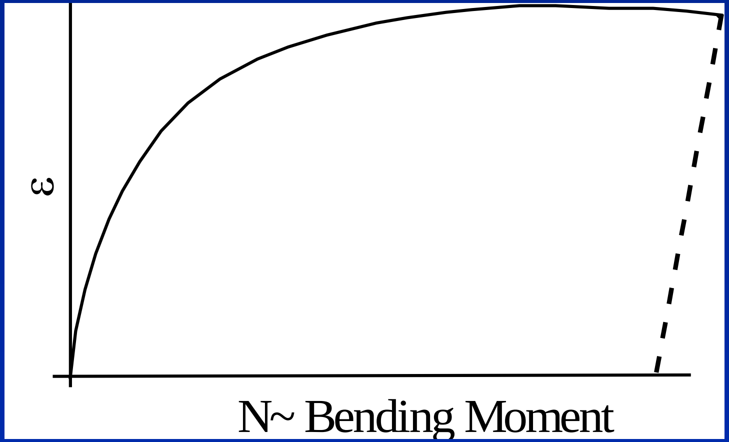
$$a_1 = \frac{8(1-\gamma^2)(1-3\gamma/8)}{3(1-\gamma/2)} \qquad a_3 = \frac{16(1-\gamma^2)}{3}$$



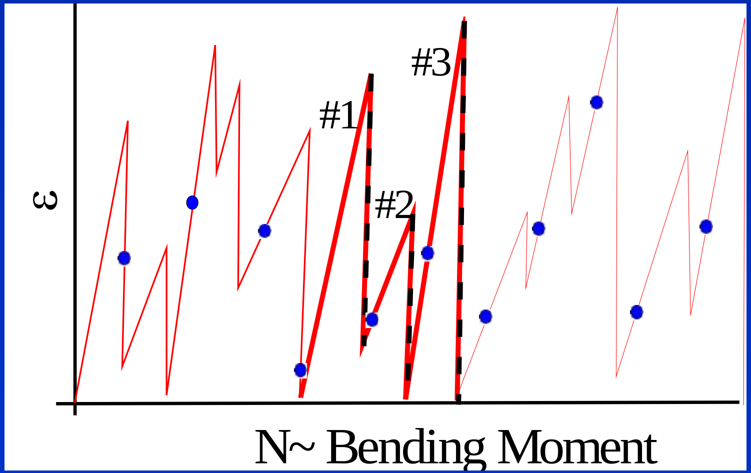
- Larger cracks have larger effect on the Young's moduli renormalization than the smaller cracks
- Less porous ceramic has larger Young's moduli

II. Making rational of local strains: EDXRD probing length scale. Possible explanation of continuous local cracking.





Macroscopic loading curve in tension



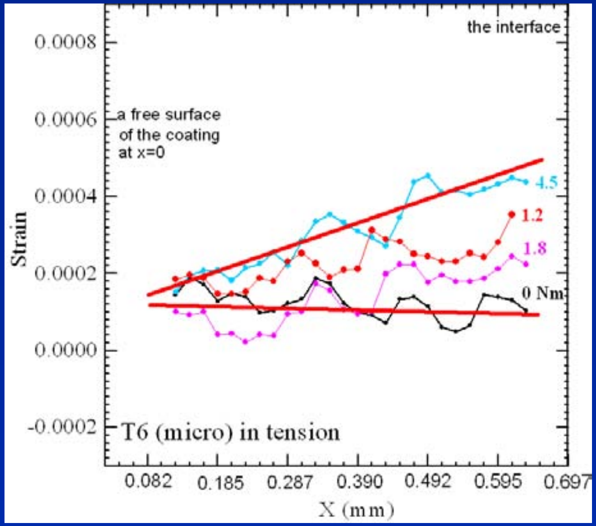
#1- Two mid size crack partly relaxes local strain

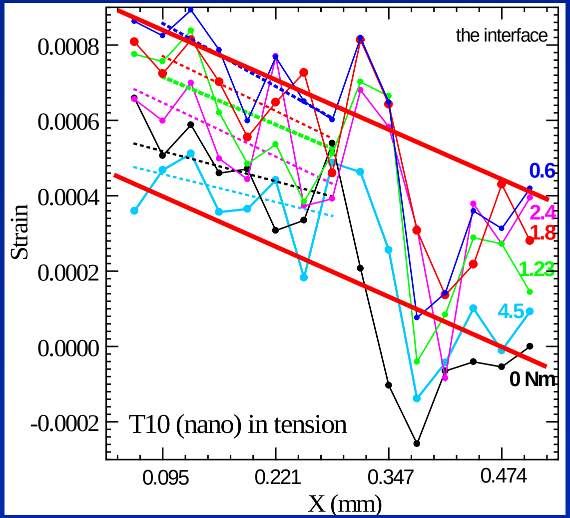
#2- One large crack completely relaxes local strain before it builds up

#3- Two cracks in vicinity of the GV concentrate local strain inside the GV

Local stain inside the GV. The EDXRD is taken at incremental loads shown by blue dots that explains stochastic strain behavior.

Invariants of local strain distribution





Local strain is a stochastic function (random sequence of observations each of which is considered as a sample of one element from a probability distribution). Stochastic behavior is an endemic property of the coatings, a signature of continuous local cracking in the GV or adjoined volumes .

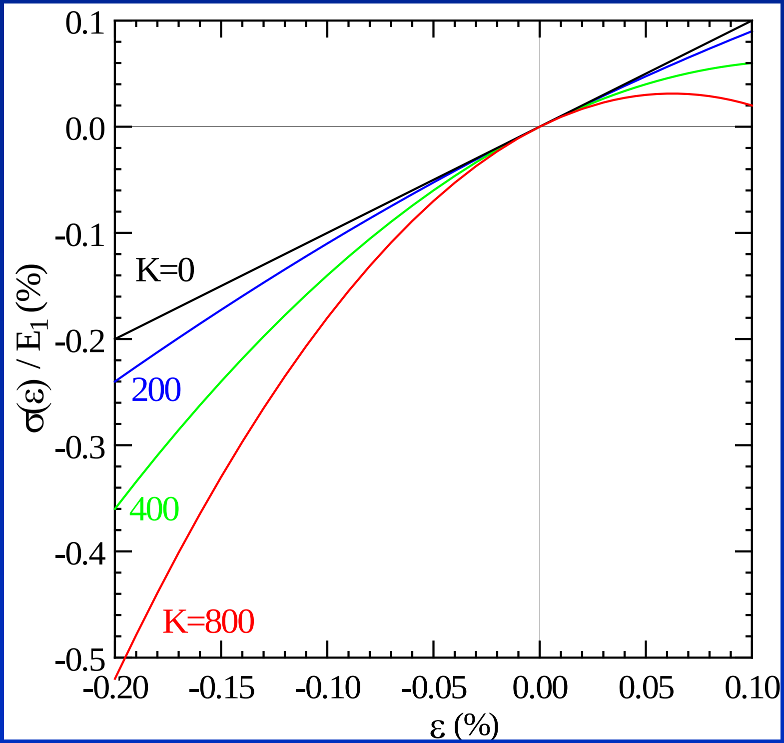
Despite of the stochastic fluctuations one can identify common trends (invariants) in the experimental data. For given value of the GV, within the specified range of low loads all experimental curves falls within the areas between two red curves.

For nano coating there are two parameters: (1) maximal local strain that the coating is capable of supporting (~0.08%) and (2) slop of the red curve (residual strain at zero load).

For micro coating one parameter seems suffice at this time: maximal local strain that the coating is capable of supporting (~0.04%).

Theory: a nonlinear stress-strain relationship

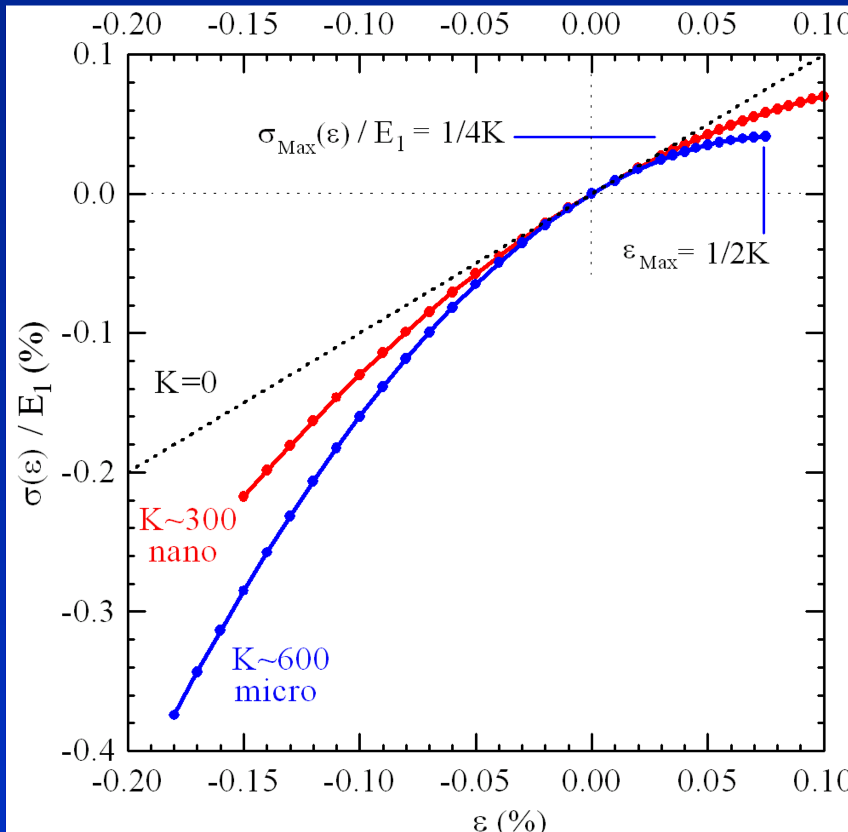
$$\sigma = E_1(\varepsilon - K\varepsilon^2) \quad for\ \varepsilon_{Yc} < \varepsilon < 1/K$$
$$\sigma = 0 \qquad elsewhare$$



- Simple, empirical relationship that is account for cracks close under compressive loads and some micro-crack density increase under tensile loads.
- *K* is usually obtained by fitting experimental δ(ε) curve for free standing coating, bending experiments (accompanied by proper simulations) or from ultrasound velocities measurements.
- Typical values of the dimensionless constant *K* characterizing stress-strain nonlinearity is
  $50 < K < 200$ for sprayed metal and
  $200 < K < 500$ for sprayed ceramics
- *K* is usually different for σ_{11} (in plain) and σ_{33} (perpendicular to the plain). It may be also different for compression and tension branches.

Source: F. Kroupa, J. of Thermal Spray Tech, v16, 84 (2007)

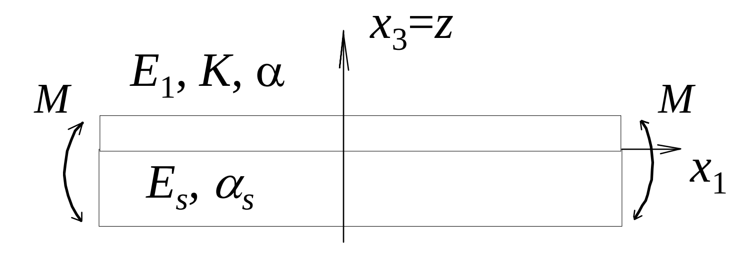
Practical application: EDXRD and modeling



Stress-strain curve of the coatings in the form $\sigma(\varepsilon)= E_1(\varepsilon-K\varepsilon^2)$ is fitted to our EDXRD data for nano(red) and micro (blue). Note that K is obtained from the tensile branches (likely is the GV-dependent) and is defined as typical maximal local strain that coating is capable of supporting: ($\sigma(\varepsilon)/ E_1$ ~0.08% for nano, and ~0.04% for micro).

Bending of beam with nonlinear coating:

- as a plain stress problem
- $\sigma(\varepsilon)= E_1(\varepsilon-K\varepsilon^2)$ in the coating
- $\sigma(\varepsilon)= E_s(\varepsilon)$ in the substrate



$$\varepsilon = (\alpha_s - \alpha)(T - T_0) = const$$

$$\varepsilon_c^{11}(z) = A(z/h) + B - \varepsilon, \quad for \quad 0 < z \le h$$

$$\varepsilon_s^{11}(z) = A(z/h) + B, \quad for -h_s \le z < 0$$

$$F(A,B) = 0 \quad \leftrightarrow \quad \int_{-h_s}^{h} \sigma(z)dz = 0$$

$$G(A,B) = 0 \quad \leftrightarrow \quad \int_{-h_s}^{h} \sigma(z)zdz = M$$

System of two nonlinear equations is solved numerically for A an B. The results for ε(z) is compared with our EDXRD mapping.

Conclusions

(1) In both n- and μ- coatings of optimal thickness the stain increases proportionally to the applied bending moment till the coatings delaminate under compressive load. Compressive yield strain is about -0.15 (-0.18)% for nano (micro) coatings.

(2) We presented first experimental data of strain profile in n- and μ- coatings under small tensile loads . The coating responses are different, indeed. The strain distribution is almost uniform across the n- coatings, while the strain relaxes towards the free surface of the μ- coatings. A maximal local strain that the coating is capable of supporting is <u>~0.08% for nano</u>, and <u>~0.04% for micro</u>.

(3) Local strain is a stochastic function. Yet, one can identify common trends (invariants) in the experimental data. One of the invariants, the maximal local strain that the coating is capable of supporting (~0.08% for nano, and ~0.04% for micro) may be used in modeling utilizing nonlinear stress-strain relationship $\sigma(\varepsilon)= E_1(\varepsilon-K\varepsilon^2)$. Detail modeling within the plain stress approximation is a work in progress.

(4) Strain mapping results were elaborated by optical and SEM microscopy. Cracks of different length scales (from micro to optically visible macro cracks) were observed in micro coating. In nano coatings the crack network is substantially less developed . Some of inclusions (partially-molten domain with α-Al_2O_3 grains) stops microcracks .

Thank you!

Acknowledgments: The financial support of Office of Naval Research under grant N000140610880 is gratefully acknowledged.
Samples were prepared by A&A Co.

Professors M. Croft[2,3] and T. Tsakalakos[1]
Drs. Z. Zhong[3], E. K. Akdogan[1], N. Jisrawi[1], and R. Sadangi[1]
L. Balarinni[1] and N. Ahmedi[1]

[1] Department of Materials Science and Engineering, Rutgers University, Piscataway, NJ 08854
[2]Department of Physics, Rutgers University, Piscataway, NJ 08854
[3]National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973

E-mail: aignatov@rci.rutgers.edu

Appendix. What the current modeling can / cannot explain

- √ Observed ε(x) trends for both n- and μ- coatings;
- √ 1/R and deflections of both coatings in tension and compression;

- ✗ Continuous fracturing behavior in tension;
- ✗ Estimated values of *K* from EDXRD in tension seem 2-3 times larger than those reported in the literature . Quantities derived from the EDXRD in tension are likely depends on probing volume (GV).
- ✗ Currently, loads are limited to those imposing elastic deformations in the substrate. Therefore, the coating fracturing in compression is not a part of the current model.